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(54) **Reinigung von Kunststoffen.**

(57) Kunststoffe werden vorteilhaft dadurch gereinigt, daß man sie mit einer alkalischen wäßrigen Lösung in Kontakt bringt, die eine anorganische Peroxidverbindung und einen Komplexbildner ohne saure Gruppen in freier oder Salzform enthält. Der Kunststoff kann hierbei als Formkörper oder in feinverteilter Form eingesetzt werden.

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Cleaning Plastic Materials

Abstract

Plastic materials are cleaned economically in that they are brought into contact with an alkaline, aqueous solution that contains an inorganic peroxide compound and a complexing agent without acid groups in a free or a salt form. The plastic material can be used, in this process, as a molded article or in a finely dispersed form.

Description

The invention relates to a process and a means for purifying plastic materials in the unprocessed and in the processed form--in particular, plastics that get in contact with chemically highly purified liquids. During the production, use--and, in particular--during storage, contaminants from container surfaces can get into the liquids so that--especially, after prolonged contact and, in particular, at higher temperatures--they are appreciably contaminated, even if contaminants on the container walls can be detected only with special methods such as neutron activation.

Highly purified liquids for analytic, diagnostic, and therapeutic purposes as well as in semi-conductor production are increasingly processed and stored in plastic containers and conveyed in plastic pipelines while, as a rule, a portion of the valuable highly purified liquid is used to rinse the lines, or the container, and must subsequently be cleaned again or rejected. Therefore, this method is very unsatisfactory.

It was discovered that highly purified liquids stored in extruded plastic containers contain heavy-metal traces that previously could not be detected in the liquid and that are detectable at the surface of the plastic material only in small traces. Precautionary cleaning of the plastic surfaces with an alkali-amine as described in "Metalloberfläche" 38 (1984) 4, pp. 163-168--in particular, p. 164--brought no improvement.

From US-A 3 908 680, a process is known for cleaning plastic contact lenses by treating them with a basic, aqueous solution of a per-compound releasing an active oxygen that is characterized in that the contact lenses are additionally treated with an acid aqueous solution of a per-compound releasing an active oxygen and, after removal from the second aqueous solution, treated with a non-ionic detergent, and then rinsed with water.

In the first and/or second solution, preferably additional chelating agents can be added--namely, preferably amino carboxylic acid compounds--whereas the acid groups can also be used in the form of their water-soluble salts. Citric acid or citrates and polyphosphates are other chelating agents mentioned. However, also with this familiar method, the problem underlying the invention could not be solved satisfactorily.

Surprisingly, it was discovered that goods results were already obtained by a one-step method for cleaning plastics yields that is characterized in that the plastic is brought into contact with an alkaline aqueous solution that contains an inorganic peroxide compound and a complexing agent without acid groups in a free or in a salt form and--to the extent necessary, contains a base.

Furthermore, the invention relates to an aqueous, alkaline cleaning solution that is characterized by a content of

- a. an inorganic peroxide,
- b. a complexing agent without acid groups, in a free form or in a salt form, and--if necessary,
- c. a base.

In a preferred embodiment of the invention, the complexing agent is an alkanolamine, although this by itself--as mentioned in the preceding--does not produce a satisfactory effect. Furthermore, it was discovered that the extrusion dye represents a possible source for the introduction of contaminants. Therefore, the presence of an oxidizing agent was needed to bring the heavy-metal traces--in particular, iron--first into an ionic form so the complexing agent can have its effect.

Here and in the following, iron is treated as a "key contaminant" because, compared to other heavy metals, it is present in the highest concentrations by far and is also difficult to remove. Experiments have shown that, as a rule, removal of the iron also eliminates the other heavy-metal contaminants.

For the complexing of the iron, the hydroxy groups--in the case of the preferred complexing agents, the alkanolamines--appear more relevant than the nitrogen atom (which appears more important for other heavy metals such as chromium). For good complex formation, two hydroxy groups are necessary that are bonded to the same nitrogen atom by way of "spacer" groupings. The "spacer" can be an alkalene group with up to 6 C-atoms that can be interrupted by oxygen atoms and nitrogen functions by which should be understood, for instance, compounds of the type of ethylene diamine-tetra-(hydroxy alkyl)-compounds.

Preferred are easily accessible alkanolamines such as the addition products of ethylene- and propylene oxide to ammonia, primary alkyl amines with 1-4 C-atoms, as well as ethylene diamine.

For higher demands of cleaning action, those kinds of compounds that can easily be obtained in a highly purified state--for instance, by sublimation or distillation--are especially preferred.

The alkanolamines show the further advantage that, not only do they not adhere to the organic substrates, but they also remove inorganic and organic contaminants adhering to them. In addition, because of their "contaminant-suspending capacity," they prevent a recontamination of the already cleaned surfaces. The preferred alkanolamine is triethanolamine. It represents a mild alkali (a 0.1 n aqueous solution has a pH value of 10.5) and causes no skin irritation at all.

As inorganic peroxide compounds, alkali peroxides can be used whereas--as with the alkanolamines--the addition of a base is not necessary. However, the use of hydrogen peroxide is advantageous. The amount of hydrogen peroxide is determined most simply by preliminary tests under the application conditions because, as is generally known, this compound is sensitive to temperature. However, it turned out that the alkanolamines that are preferably used as complexing agents exert a stabilizing effect.

At temperatures up to about 80°C, concentrations of at least about 5% by weight, relative to the finished cleaning solution, are beneficial. Smaller concentrations frequently require a longer exposure time; generally, higher concentrations are necessary only with stronger contaminations of the substrate.

Advisedly, the alkaline cleaning solution has a pH value in the range of 7.5 to 12--preferably, 8 to 10. Because alkanolamines have an alkaline reaction, the addition of another base is not always necessary when they are used. However, the addition of an aqueous ammonia solution is frequently beneficial while, on the contrary, the amount of the more expensive alkanolamine can be reduced. The most favorable combination in an individual case can be determined by simple preliminary tests.

A preferred embodiment of the invention consists in that the plastic is used in a finely dispersed form so that the contaminants can be extracted by the cleaning solution according to the invention.

The cleaning process according to the invention can be used over a wide temperature range. In the cleaning of molded articles, one acts according to the temperature sensitivity of these molded articles and one operates, for instance, in a room temperature range of up to 120°C--preferably, about 50°C. If a finely distributed plastic is extracted, one advantageously chooses a higher temperature--advisedly about 80 - 120°C. Generally, shorter treatment times are sufficient at a higher temperature.

However, here, the increased disintegration of the peroxide compounds has to be taken into consideration--therefore, possibly adding them subsequently in metered dosages or using them right from the beginning in an adequate concentration.

The cleaning method according to the invention can generally be applied to all plastics. It also works superbly with hydrophobic plastics that are used in the packaging field, such as polyethylenes, polypropylenes, polyvinyl chlorides, and polyesters. However, it can also be used with advantage for the so-called high-performance plastics such as polyacetals, polyphenylene sulfides, polyether ketones, and especially fluoro-carbon polymers.

As mentioned in the beginning a single-step treatment is generally adequate, in contrast to the process familiar from DE-C 24 43 147. A pre-treatment, or optionally also a post-treatment, with acid solutions should thereby not be excluded. For instance, a hydrofluoric-acid after-treatment is suitable, while peroxides and optionally auxiliary agents such as surfactants can be added to the HF solution.

A mixture of the following composition (in percentage by weight) has proved to be effective: ?

89.5% water,
10.0% H_2O_2 (30%), and
0.5% HF (50%).

If necessary, residual iron contaminants can be extracted by that kind of aftertreatment.

In the process according to the invention, also other additives can added to the alkaline solution, such as other complexing agents, surfactants, buffers, or the like. As surfactants, first of all non-ionic surfactants are suitable such as addition products of ethylene- and/or propylene oxide to long-chain alcohols, alkylphenols, and the like. Amounts up to 400 ppm--preferably, 100-300 ppm; above all, about 200 ppm, relative to the finished cleaning solution--are effective. Hereby the wetting of the surfaces is accelerated without the development of unwanted foaming.

According to the invention, also a multiple treatment of the substrate is suitable if a considerable migration of contaminants from the depth of the plastic can be determined--for instance, after heating the substrate.

Also the addition of organic solvents is possible even if, generally, not advantageous because their recovery is expensive.

Especially preferred embodiments of the invention are explained in more detail in the following examples.

In the examples, highly purified chemicals are used to guarantee that no heavy metals that falsify the measured results are introduced by these chemicals. Therefore, these examples have the character of "an ideal" because, in practice, technical grades of the used chemicals can be applied because of the mentioned dirt-suspending capacity of the preferably used alkanolamines.

All experiments are carried out with consideration of the common rules of trace analysis. For instance, bidistilled water and triethanolamine distilled in a high vacuum were used; hydrogen peroxide and ammonia solution were commercial "VLSI" grades (Merck Company, Darmstadt). The iron was determined by atomic absorption spectrometry (atomic absorption spectrometer of the Varian Company, Spectraa 400, as well as a graphite furnace and a sample stage GTA 96) at 248.3 nm, slit width: 0.2 nm; background correction: deuterium lamp; injection volume: 20 μ l; detection limit: 0.3 ng/ml; linear calibration range: 0 to 13 ng/ml.

A copolymer, serving as a substrate, consisted of 96% by weight of tetrafluoroethylene and 4% by weight of perfluoro-n-propylvinyl ether with a melt flow index of 2g/10 min, determined according to ASTM D1238-57 T (at 372°C and 5 kg load) with an iron content of 500-550 ng/g copolymer.

As follows from the following experiments, the largest portion this iron content is present in the interior of the plastic, because repeated treatment--without interim heating of the plastic material--yielded only relatively small amounts of extracted iron.

Examples 1-7

50 g of plastic granulate with an average particle size of 16.9 mm³ were left standing for 60 minutes with 25 ml of cleaning solution of the composition indicated in Table 1. Table 1, below, shows the results.

In Table 1, comparison examples V1-V3 are contained in which one of the components of the cleaning solution according to the invention is missing.

The composition of the cleaning solution is defined as follows: "parts" are parts by weight, whereas the hydrogen peroxide is used as a 30% aqueous solution and the ammonia as a 25% aqueous solution.

The concentration of triethanolamine (TEA) is indicated in ppm. The extraction result is indicated in ng iron/g of plastic.

The comparison examples V1 and V2 show that an ammoniacal TEA solution has only a relatively small extraction effect.

Beispiel	Teile			TEA [ppm]	Fe [ng/g]	
	H ₂ O	H ₂ O ₂	NH ₃		30 min	60 min
V1	4	-	1	500	0,56	0,69
V2	4	-	1	1000	0,49	0,62
V3	3	1	1	---	0,82	1,07
1	3	1	1	500	1,04	1,29
2	3	1	1	1000	1,10	1,41
3	3	1	0,5	1000	1,02	1,39
4	4	1	1	1000	0,91	1,32
5	4	1	1	10000	1,58	2,01
6	5	1	1	1000	0,82	1,21
7	6	1	1	1000	0,92	0,96

Comparison example V3 shows that an ammoniacal hydrogen peroxide solution produces clearly worse extraction results than the cleaning solutions according to the invention.

The examples according to the invention show that, according to expectation, the cleaning effect depends on the concentration. This counts, above all, for TEA but, with the available measuring device, no reliably reproducible data are possible at still higher concentrations. However, higher concentrations of TEA are advantageous not only with respect to the cleaning effect but also with respect to the stabilization of the hydrogen peroxide.

Example 8

One proceeds according to example 3 but extracts for 75 minutes by which a final concentration of extraction iron of 1.5 ng/g of plastic is attained. By renewed application of a fresh solution, 0.47 ng/g was extracted after 60 minutes.

Example 9

Example 4 is repeated, but the sample is shaken with about 100 Hz during the extraction. After 30 minutes, 3.59 ng Fe/g of plastic are extracted.

Examples 10-12

Little bottles, molded from the copolymer, with a holding capacity of 50 ml are filled with the cleaning solution used in example 4 and stored at different temperatures for 30 and 60 minutes, respectively. Table 2 shows the extraction results.

Beispiel	Temperatur [°C]	Fe [ng/g]	
		30 min	60 min
10	Raumtemperatur	0,73	1,47
11	50	1,30	1,81
12	80	1,83	2,35

Example 13

Example 11 is repeated but the little bottles are dipped up to 3/4 of their height into an ultrasonic bath. After 30 minutes, 1.58 ng Fe/g of plastic are extracted, and after 60 minutes, 2.31 ng Fe/g of plastic are extracted.

Example 14-16

Example 3 is repeated, but increasing amounts of a non-ionic surfactant (commercial product: TRITON X 100®) are added. Table 3 shows the results.

Beispiel	Tensid [ppm]	Fe [ng/g]	
		30 min	60 min
3	0	1,02	1,39
14	100	1,51	1,59
15	200	1,40	1,67
16	400	1,83	2,42

With an increasing addition of surfactant, increasing foam formation occurs. In addition, faster decomposition of the hydrogen peroxide was observed in example 16.

Example 17-20

The little bottles used in examples 10-12 are filled, at room temperature, with 25 ml of the cleaning solution indicated in Table 4, and stored for 30 and 60 minutes, respectively. The extracted chromium portion [ng(Cr)], relative to the amount of plastic used [g], are indicated in Table 4. V4 is a comparison example with water.

Beispiel	Teile			TEA [ppm]	Cr [ng/g]	
	H ₂ O	H ₂ O ₂	NH ₃		30 min	60 min
17	3	1	1	1000	0,70	0,95
18	3	1	0,25	1000	0,40	0,59
19	4	1	1	1000	0,54	0,72
20	5	1	1	1000	0,45	0,65
V4	1	-	-	---	0,031	---

For Table 4, the same definitions apply as for Table 1.

Patent claims

1. Method for cleaning plastics, characterized in that the plastic is brought into contact with an alkaline aqueous solution that contains an inorganic peroxide compound and a complexing agent without acid groups in a free form or in a salt form and, if necessary, a base.
2. Method according to claim 1, characterized in that the plastic is used as a molded body that is cleaned at its surface.
3. Method according to claim 1, characterized in that the plastic is used in a finely distributed form and that the impurities are extracted.
4. Aqueous-alkaline cleaning solution, characterized by a content of
 - a. an inorganic peroxide
 - b. a complexing agent without acid groups in a free or salt form, and--if necessary
 - c. a base.
5. Solution according to claim 4, characterized in that the complexing agent is an alkanolamine.
6. Solution according to claim 4 or 5, characterized in that the complexing agent is a triethanolamine.
7. Solution according to one or more of the claims 4-6, characterized in that the peroxide is a hydrogen peroxide.
8. Solution according to one or more of the claims 4-7, characterized in that the solution contains a surfactant.

